

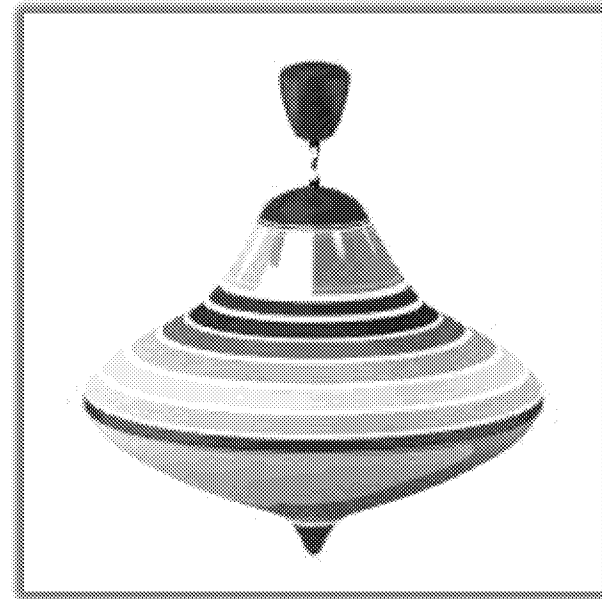
Ask The Expert Webinar Series

**TestAmerica**

THE LEADER IN ENVIRONMENTAL TESTING

# Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP) Assay

Karla Buechler – Corporate Technical Director



# TOP Assay - Outline

## Introduction to PFASs

What are PFASs?

Formation/Toxicity and Risk

Regulatory Review

## The TOP Assay

Background

What is the TOP assay

How does it work?

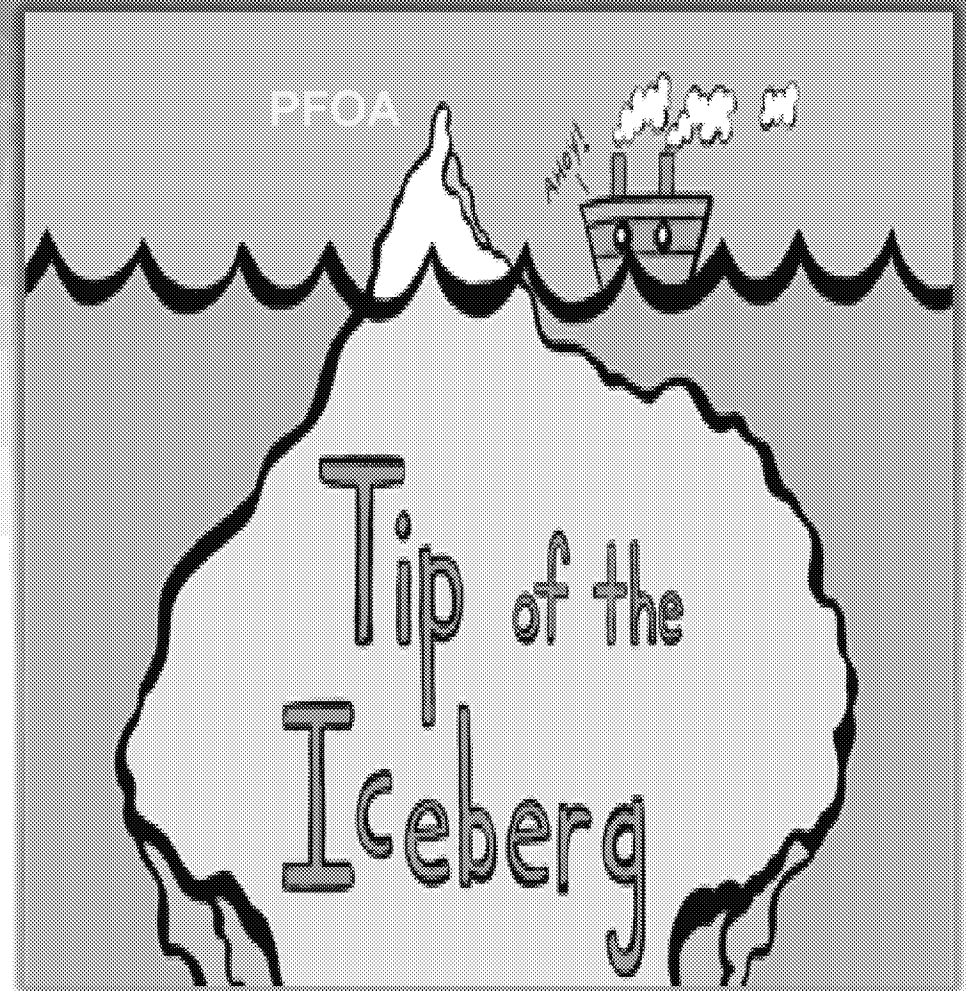
The chemical reaction

What do the results mean?

What are the limitations?

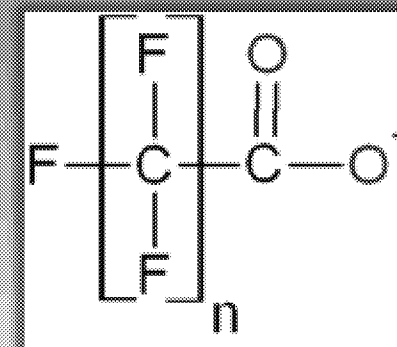
Future Concerns

Capabilities and Questions?

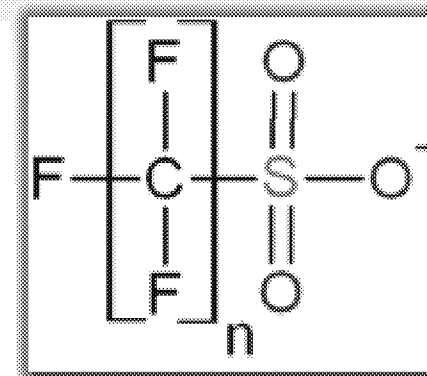


# Briefly - What are PFASs?

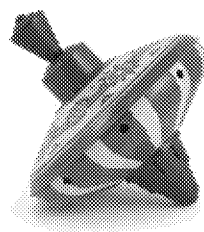
- Class of synthetic compounds containing **carbon** chains with **fluorine** attached to these chains.
- The **C-F** bond is the shortest and the strongest bond in nature.
- PFC – Subset of PFAS completely fluorinated compounds. PFOS and PFOA are PFCs (no hydrogen atoms)
- **PFAAs – Perfluoroalkyl acids – 2 classes PFCAs and PFSAAs** ★
- **PFAS do not degrade BUT they do biotransform**



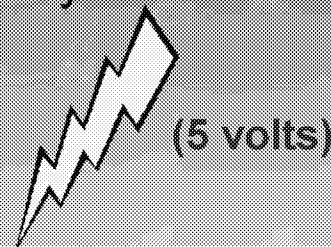
Perfluoroalkyl Carboxylate



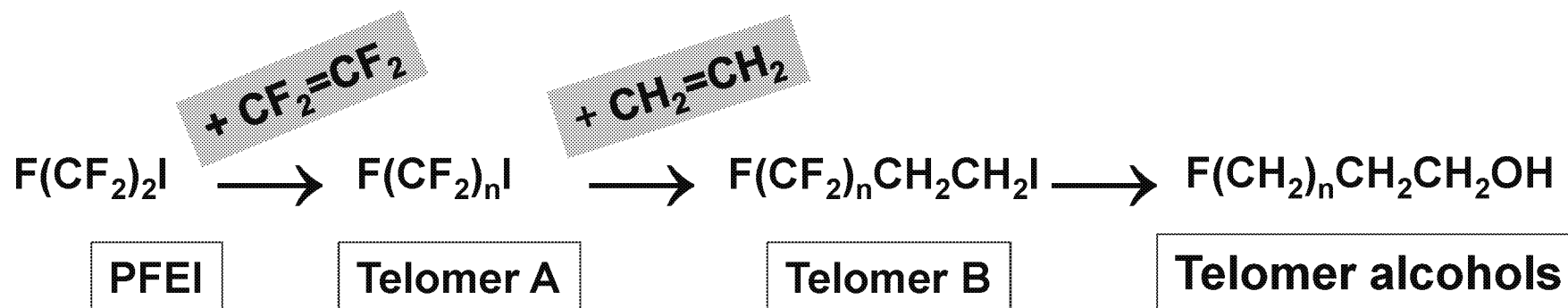
Perfluoroalkyl Sulfonate



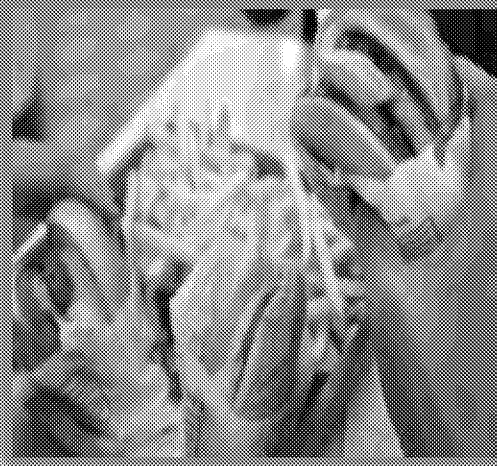
- **ECF Reaction:** Process yields a mixture of B/L isomers



- **Telomer Reaction:** Process yields 100% linear isomers  
(Synthesis of building blocks leading to fluorotelomer alcohols)



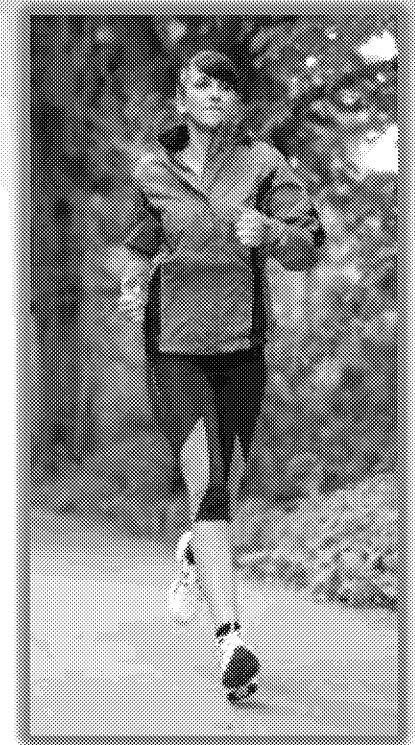
# Exposure, Toxicity and Risk



- Major source of non-occupational exposure to humans is from food and air (predominately fish consumption)
- Human and wildlife exposure can continue even though the chemicals are no longer in use, due to persistence.
- PFOS and PFOA have half-lives in humans ranging from 2 to 9 years, depending on the study.
- PFOA associated with liver, pancreatic, testicular, and mammary gland tumors in laboratory animals. PFOS causes liver and thyroid cancer in rats
- PFOA and PFOS are likely carcinogenic in humans. Pathways are being studied.

# PFAS – Regulatory Timeline

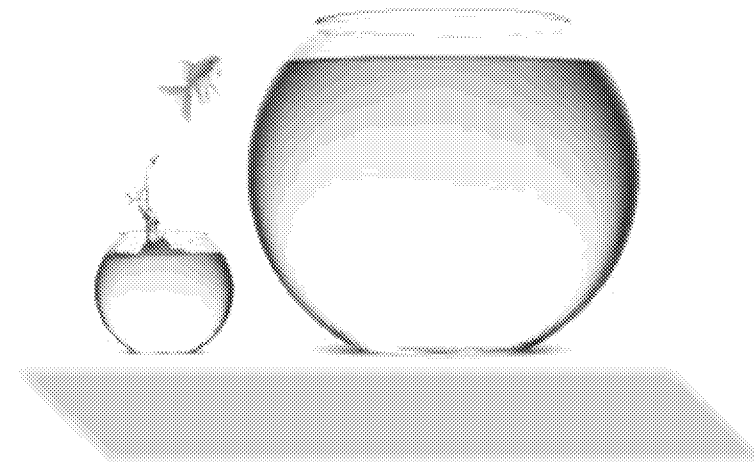
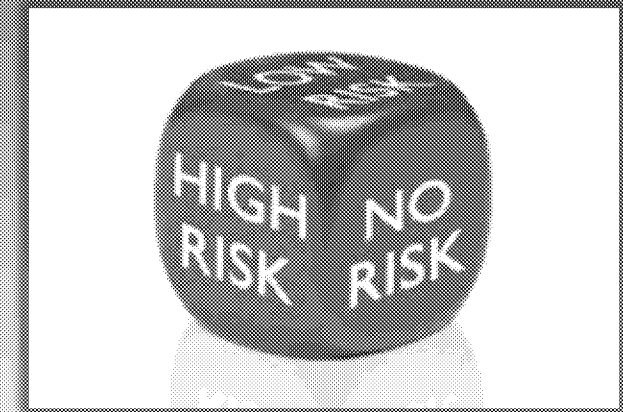
When	Who	What Happened
1980s	EU	Groundwater directive to prevent discharge of PFOS
2002	US EPA	Initiated voluntary phase out of PFOS
2002	3M	Discontinued making PFOS (7 other makers complied)
2006	US EPA	Announced 2010 (95%)/15(100%) PFOA Stewardship Program
2008	Canada	Regulated and prohibited PFOS imports to Canada
2009	UN	Stockholm Convention - adds PFOS to Annex B
2010	US EPA	2010 PFOA Stewardship program - must reduce PFOA use by 95%
2015	US EPA	Must 100% eliminate the use of PFOA by December 31, 2015.
May 2016	US EPA	PFOS and PFOA life time health limits reduced to 70 ppt each or the total if both are present.
Sept 2016	NJ	DWQI proposed PFOA drinking water MCL of 14 ppt



What started happening in 2016?

# What is Risk? Why Do We Care About PFOA?

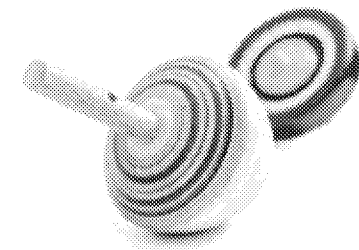
- Risk = one in one million risk of cancer from a lifetime exposure with no adverse effects
- NJ recommended health based MCL based on cancer and non-cancer endpoints = 14 ppt
- Production and use of PFOA in U.S. phased out
- Exposure continues due to persistence, biotransformation of precursor compounds and manufacturing abroad



# Polyfluorinated — PFAA Precursors



- Thousands of PFAS are used in industrial and consumer products
- Some biotransform to make PFAAs
- Some are fluorotelomers
- Most are ionic either positive, negative or both
- Fate and transport — complex process



# How Do Other PFAS Become PFOA?



Primarily 2 mechanisms:

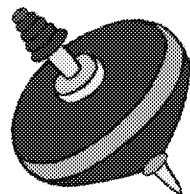
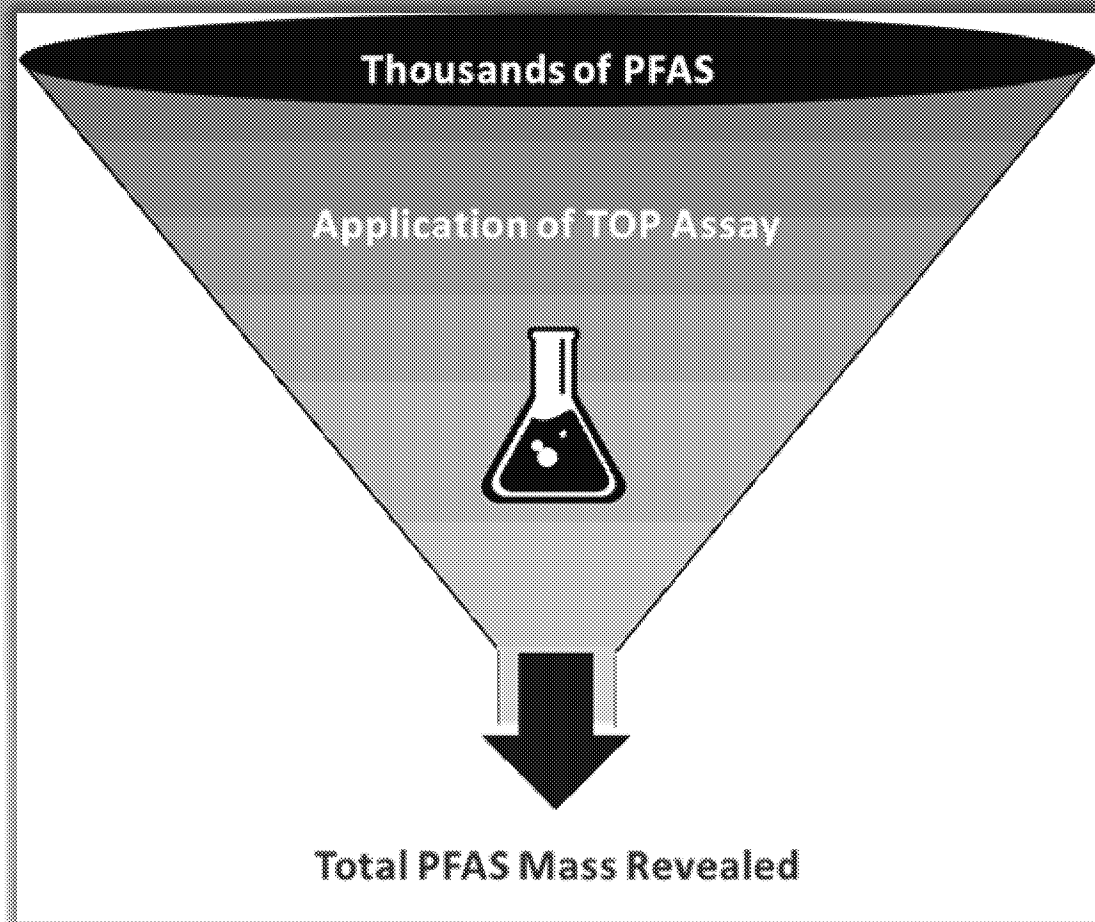
- Abiotic transformation of PFAA precursors sulfonamido and fluorotelomer precursors oxidize to form PFCAs
- Aerobic biotransformation of fluorotelomer precursors to form PFCAs
- Other biological mechanisms exist

# Discrete PFAAs and Precursors

Compound Name	Abbreviation	CAS #
<b>PFAAs - Perfluoroalkylcarboxylic acids (PFCAs)</b>		
Perfluoro-n-butanoic acid	PFBA	375-22-4
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3
Perfluoro-n-hexanoic acid	PFHxA	307-24-4
Perfluoro-n-heptanoic acid	PFHpA	375-85-9
<b>Perfluoro-n-octanoic acid</b>	<b>PFOA</b>	<b>335-67-1</b>
Perfluoro-n-nonanoic acid	PFNA	375-95-1
Perfluoro-n-decanoic acid	PFDA	335-76-2
Perfluoro-n-undecanoic acid	PFUdA	2058-94-8
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1
Perfluoro-n-tridecanoic acid	PFTTrDA	72629-94-8
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7
Perfluoro-n-hexadecanoic acid	PFHxDA	67905-19-5
Perfluoro-n-octadecanoic acid	PFODA	16517-11-6
<b>PFAAs - Perfluorinated sulfonic acids (PFSAs)</b>		
Perfluoro-1-buthanesulfonic acid	PFBS	375-73-5
Perfluoro-1-hexanesulfonic acid	PFHxS	355-46-4
Perfluoro-1-heptanesulfonic acid	PFHpS	375-92-8
<b>Perfluoro-1-octanesulfonic acid</b>	<b>PFOS</b>	<b>1763-23-1</b>
Perfluoro-1-decanesulfonic acid	PFDS	335-77-3
<b>Precursors to PFAAs - Perfluorinated sulfonamides (FOSAs)</b>		
<b>Perfluoro-1-octanesulfonamide</b>	<b>FOSA</b>	<b>754-91-6</b>
N-ethylperfluoro-1-octanesulfonamide	EtFOSA	4151-50-2
N-methylperfluoro-1-octanesulfonamide	MeFOSA	31506-32-8
<b>Precursors to PFAAs - Perfluorinated sulfonamidoacetic acids (FOSAAs)</b>		
N-ethylperfluoro-1-octanesulfonamidoacetic acid	EtFOSAA	2991-50-6
N-methylperfluoro-1-octanesulfonamidoacetic acid	MeFOSAA	2355-31-9
<b>Precursors to PFAAs - Fluorotelomer sulfonates (FTSs)</b>		
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2 FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2 FTS	39108-34-4

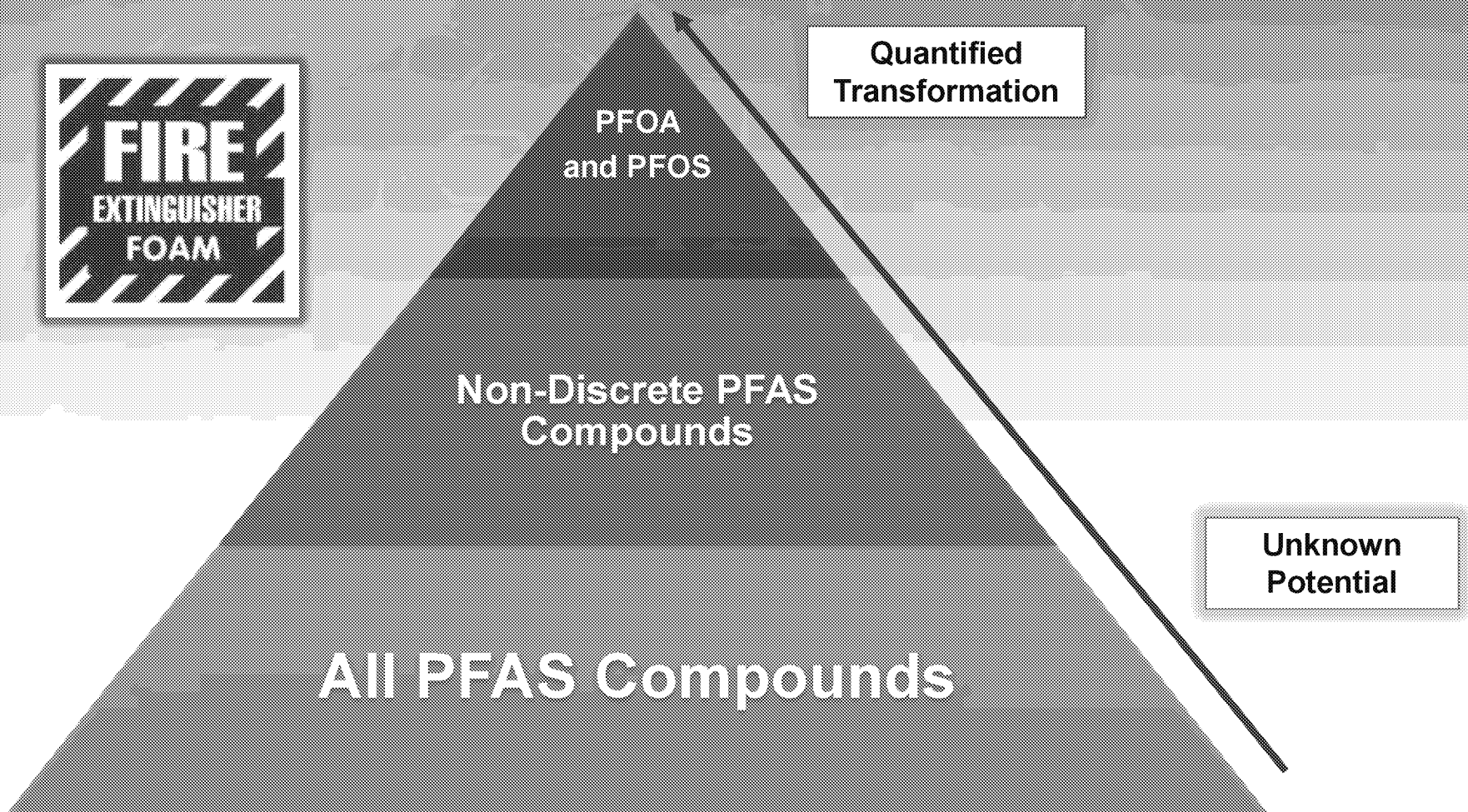
# What is the TOP Assay?

- A new PFAS sample preparation technique
- Conceptually simple chemistry
- Used in conjunction with 537M (Not 537) – combines pre and post oxidation results
- Indicates presence of unidentified PFAS in water, sediment and soil

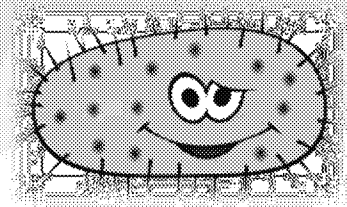
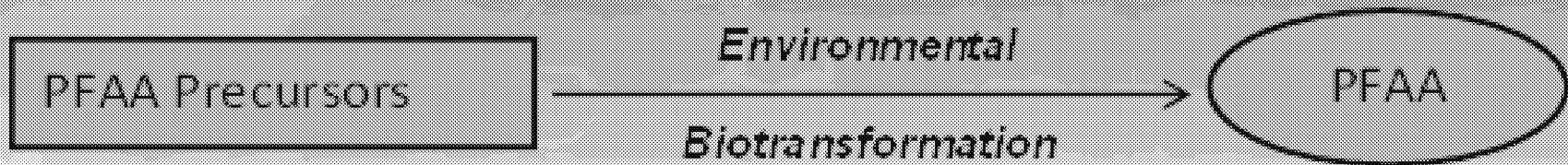


Houtz, Erika, and David L. Sedlak. 2012. Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science and Technology* 46: 9342-9349.

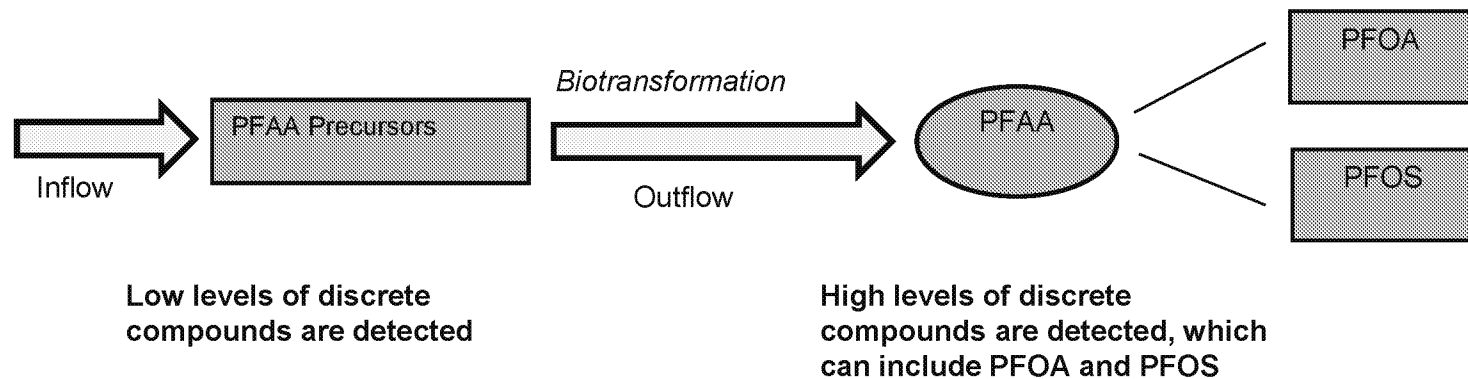
# Potential PFAS Transformation



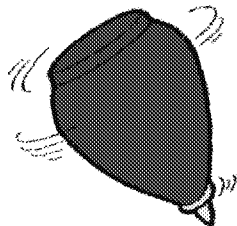
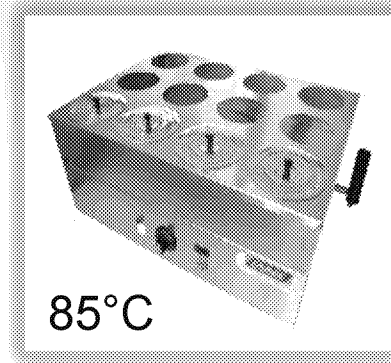
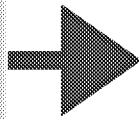
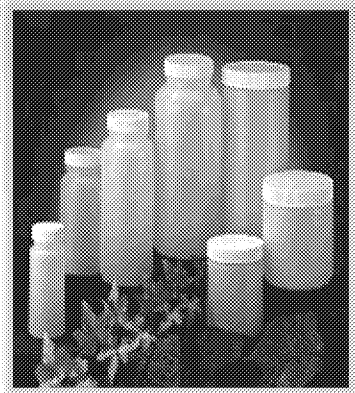
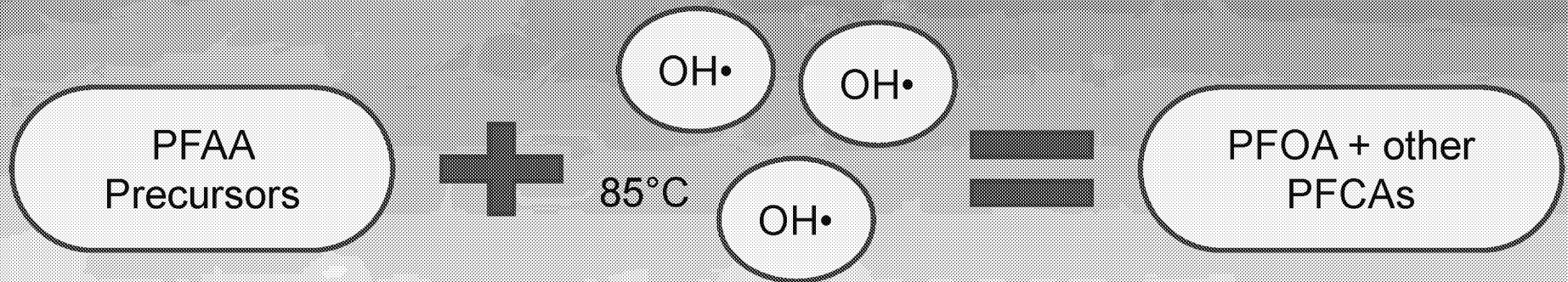
# How Does it Work in the Environment?



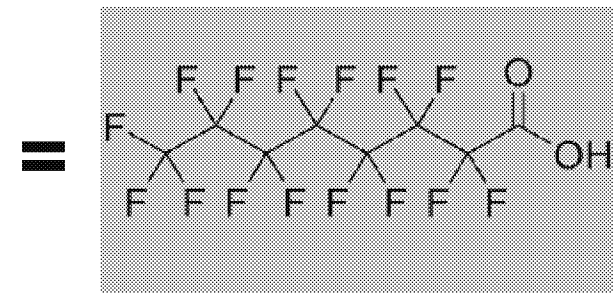
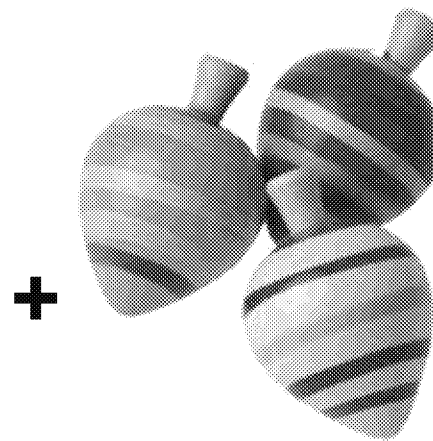
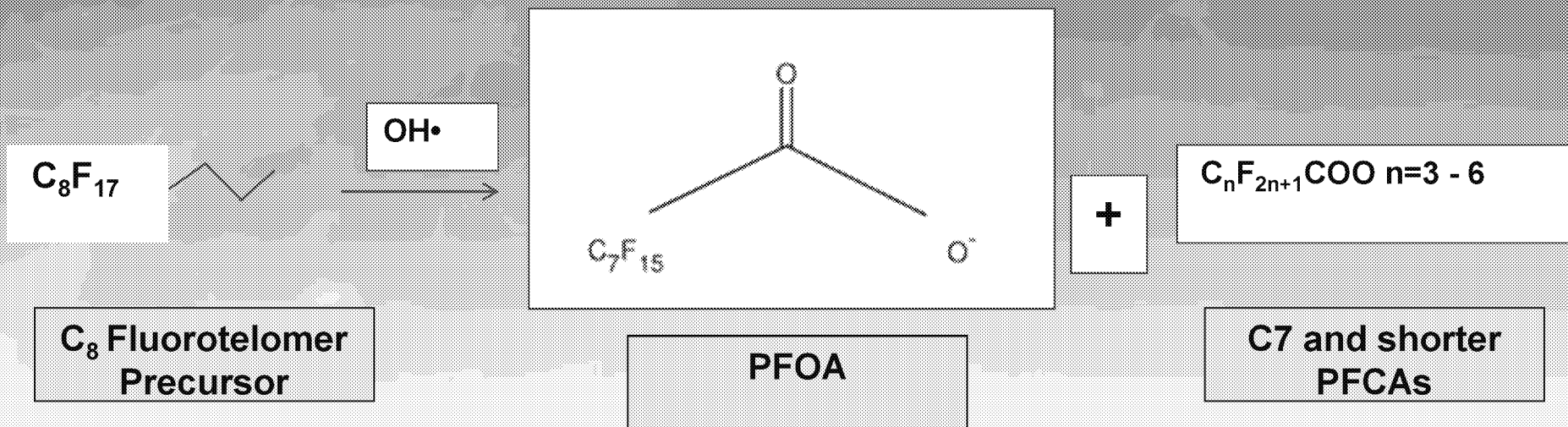
Give me an example:



# TOP – How Does it Work in the Laboratory?



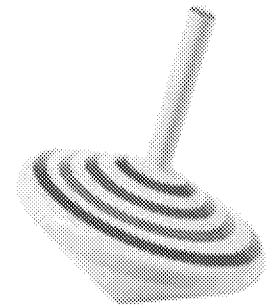
# A Closer Look at the Chemistry



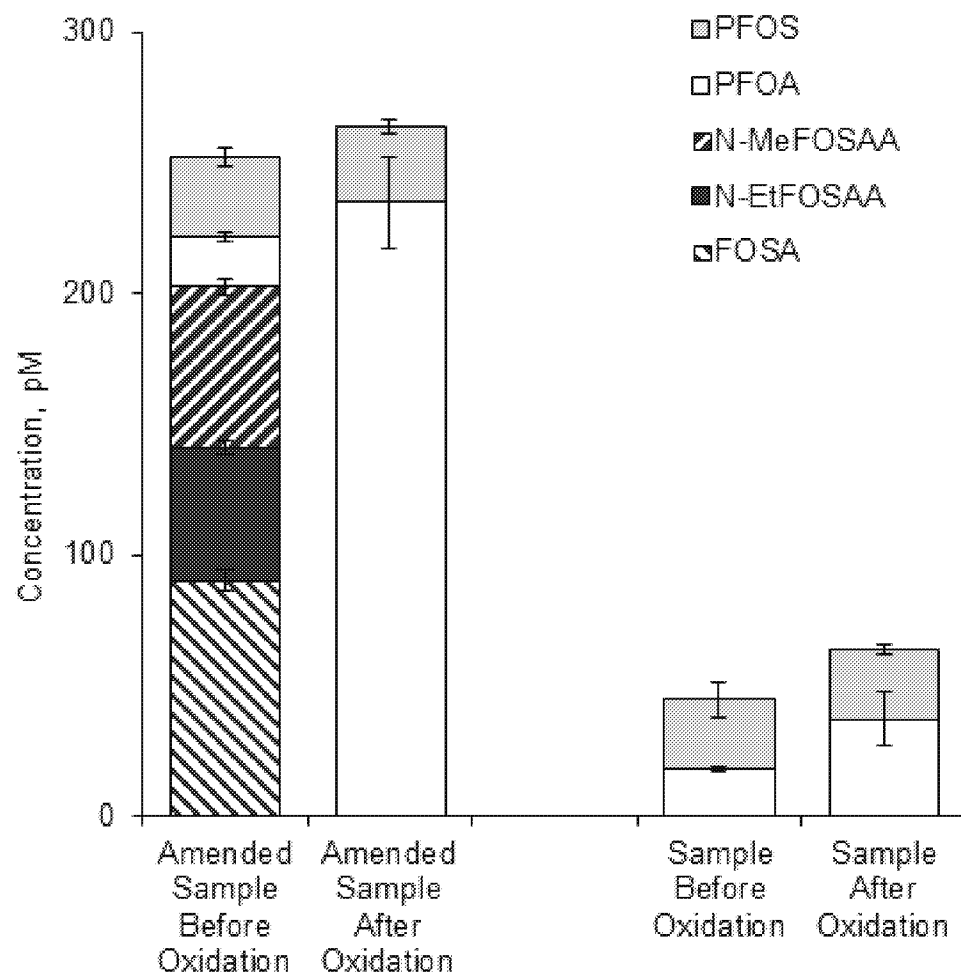
# What Do the Results Mean?

## TOP Assay measures total PFCA

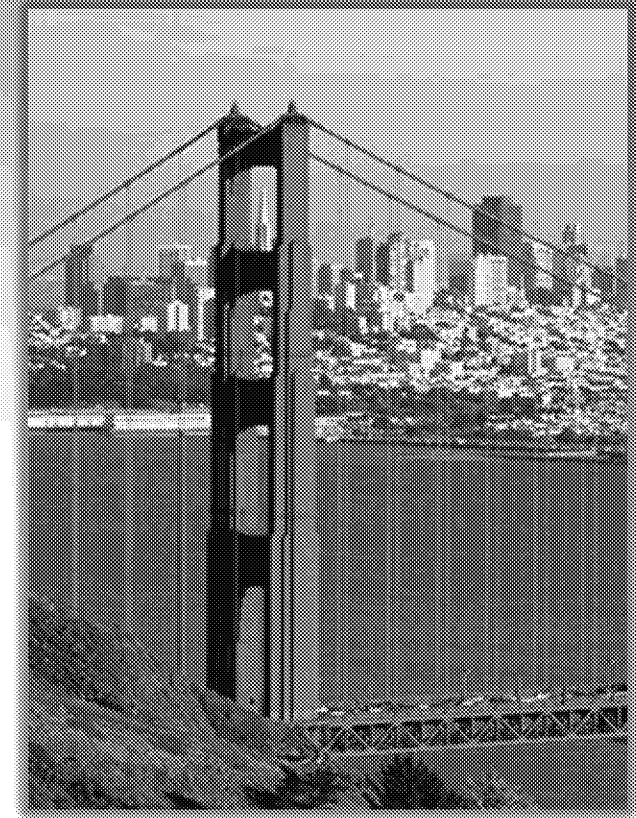
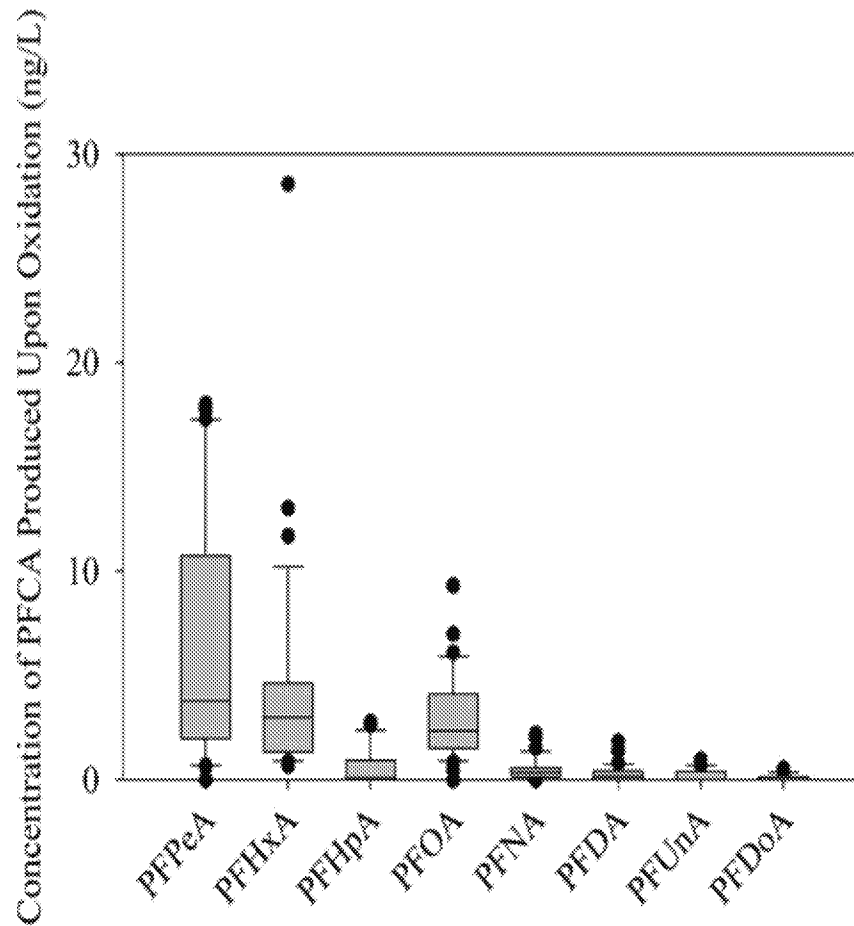
Precursor	Pre - TOP	Post - TOP	% Oxidation
★ FOSA	32.68	ND	100%
MeFOSAA	19.38	ND	100%
EtFOSAA	18.83	ND	100%
6:2 FTS	31.69	ND	100%
8:2 FTS	26.37	ND	100%
PFCA	Pre – TOP	Post - TOP	Total
PFBA	24.94	27.16	109%
PFPeA	23.38	28.55	122%
PFHxA	26.49	34.87	132%
PFHpA	23.10	25.14	109%
★ PFOA	23.72	58.71	248%
	Total 122	Total 174	



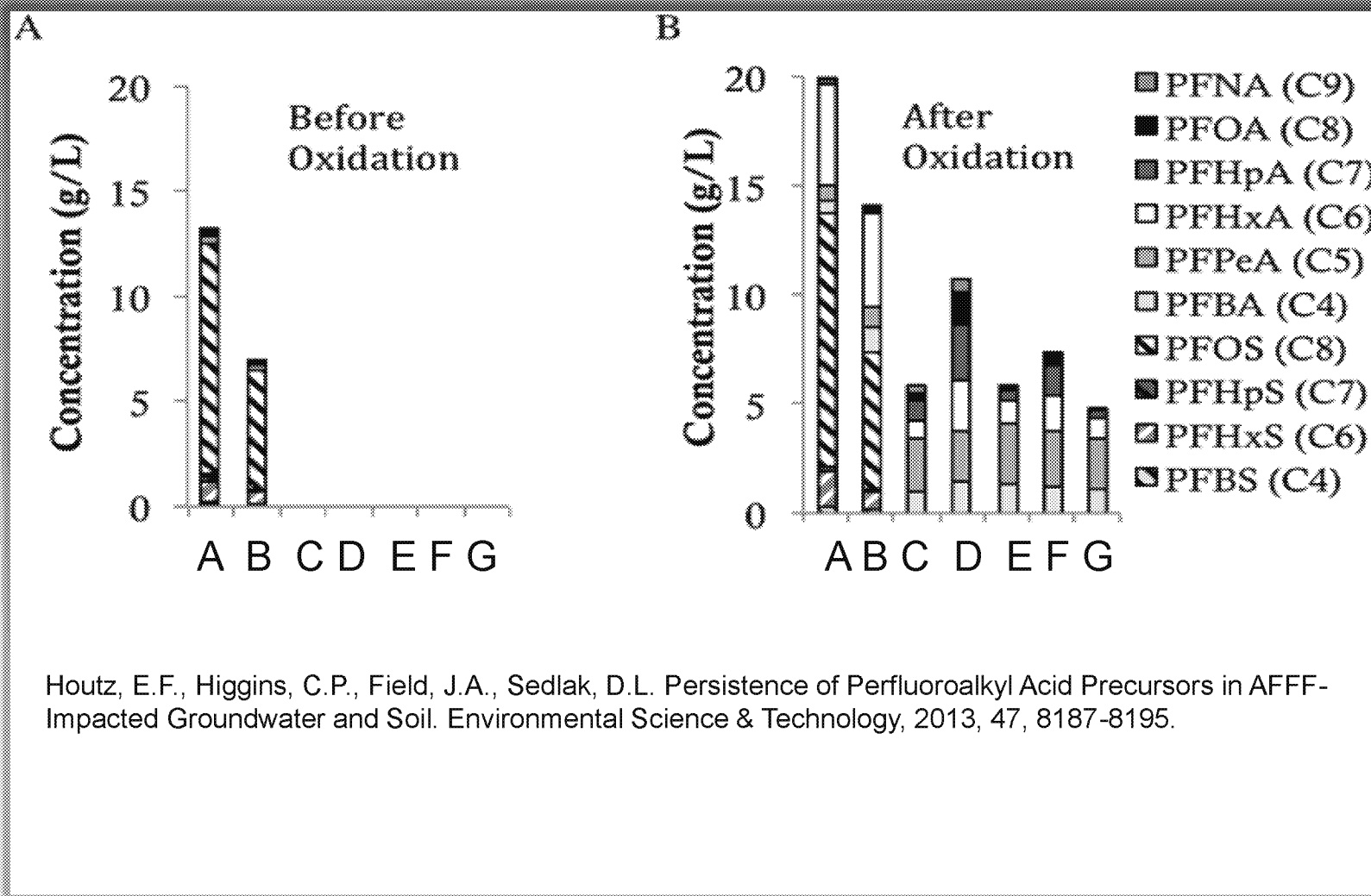
# Urban Runoff – San Jose, CA



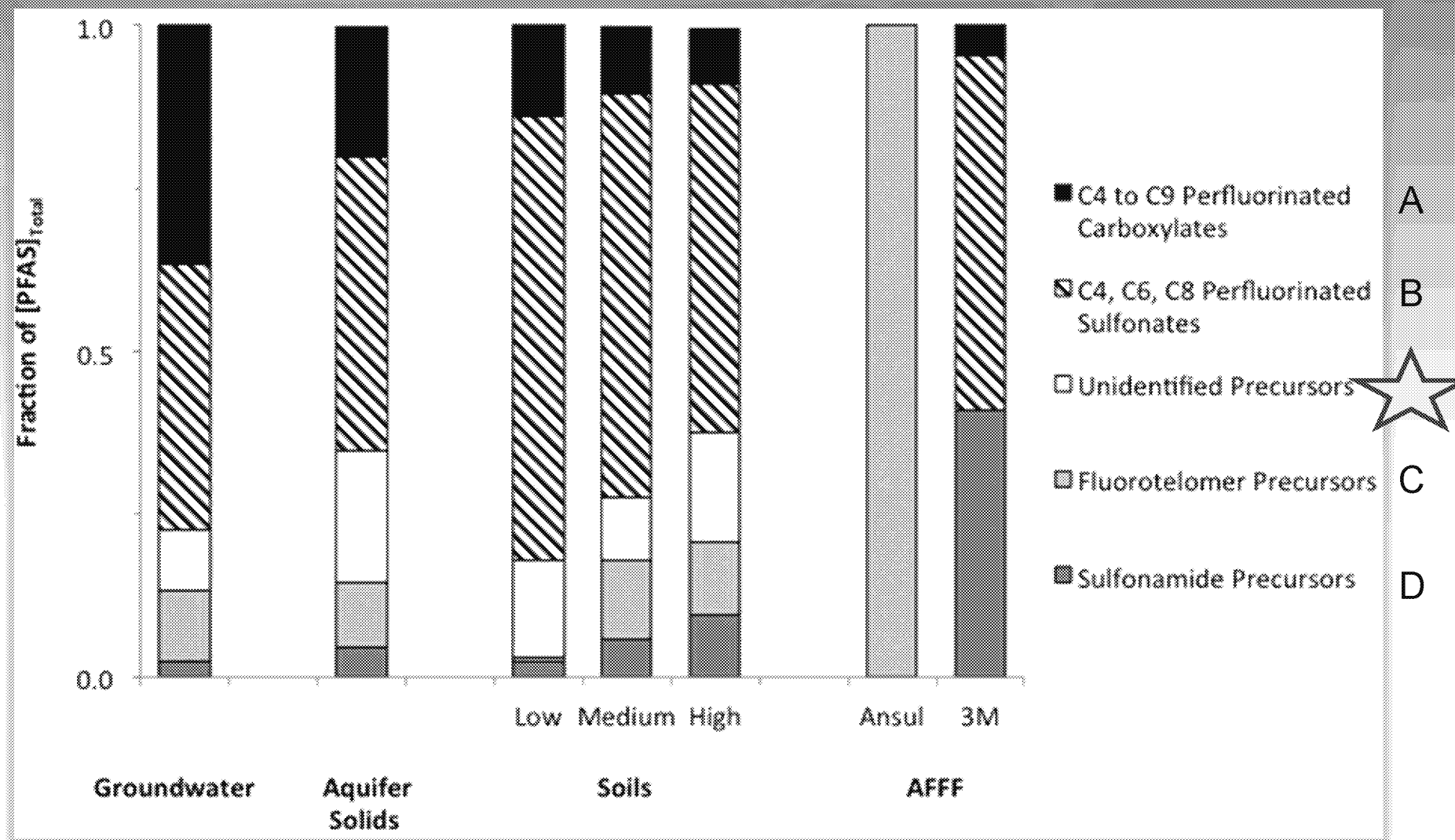
# Application #1 – Urban Runoff from SF Bay Area

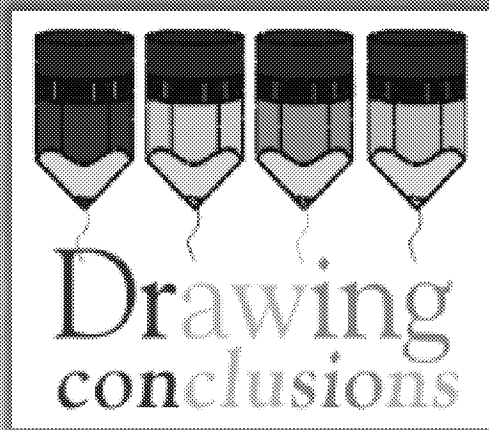


# App #2 – AFFF Formulations

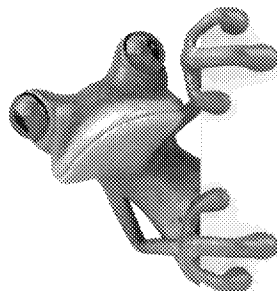


# Application #3 – AFFF Impacted Groundwater and Soils

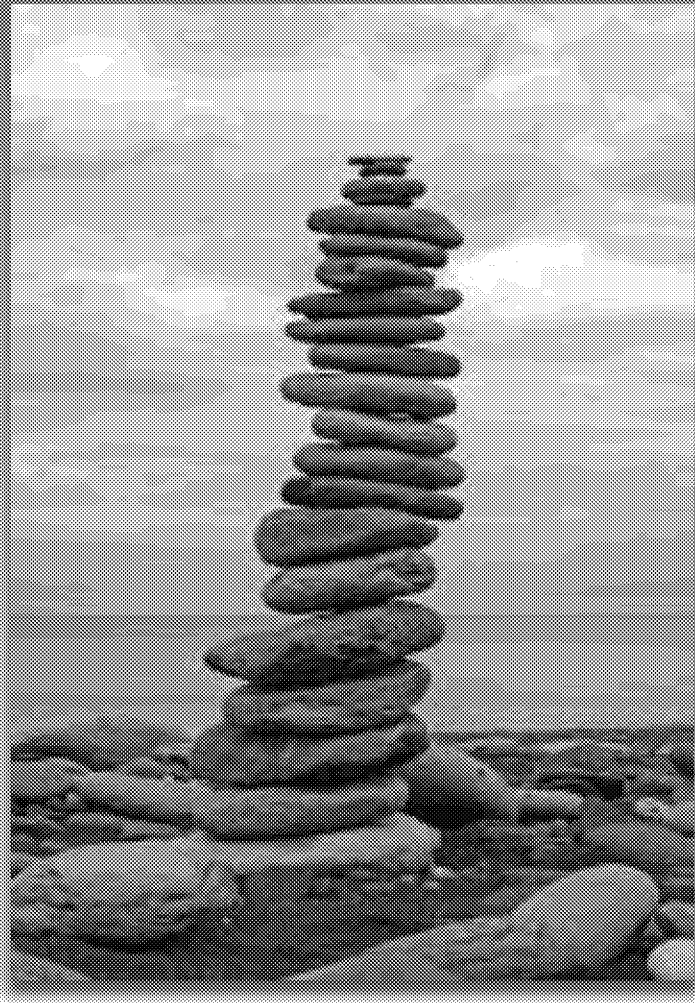




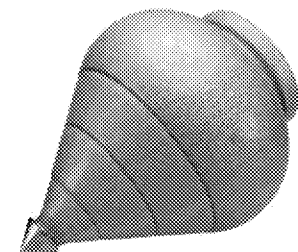
A lesson ...  
... in jumping to  
CONCLUSIONS



- PFAA precursors are present in environmental samples and many AFFF products
  - Implies treatment strategies must remove precursors and end points
- Presence impacts our treatment strategies and our risk assessments
  - Potentially increases future risk as precursors are biotransformed
- Presence impacts our decisions for AFFF formulations
  - AFFF manufacturers should reduce the content of PFOA etc.

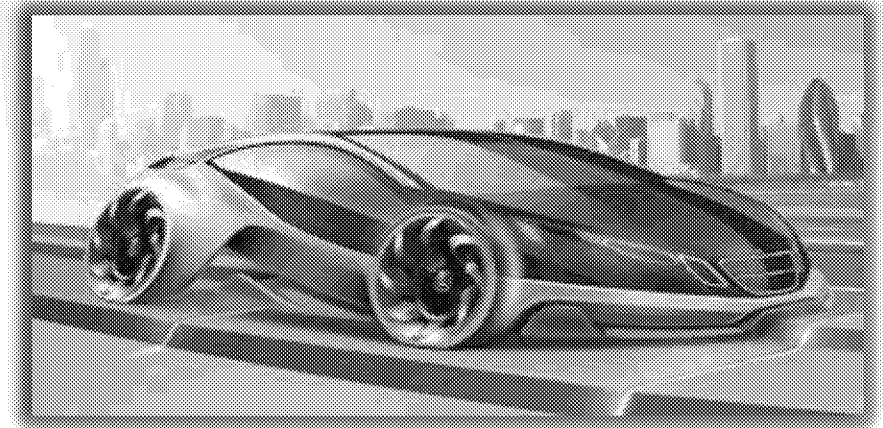


- TestAmerica Sacramento is EPA approved for Method 537 in drinking water and ISO 25101 in NYS
- Sacramento is QSM 5.1 Table B-15 approved for Method 537M
- Sacramento, Denver and Burlington Labs are NELAP approved for Method 537M.
- 8 LCMSMS instruments capable of PFAS testing
- Sacramento has successfully implemented the TOP Assay



# Future Concerns

- We need a consensus “best” method.
- Analyte lists are growing for discrete methods, may lead to forensics.
- LC PFASs are being replaced by SC PFASs and little is known about the toxicity
- On-going data variability must be improved
- We need an effective field screening technique.



- Houtz, E.F.; Park, J-S. Sutton, R. Sedlak, M. Poly- and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. *Water Research*, 2016, 95, 142-149.
- Harding-Marjanovic, K.; Houtz, E.F.; Yi, S.; Field, J.A.; Sedlak, D.L.; Alvarez-Cohen, L. Aerobic biotransformation of Fluorotelomer Thioether Amido Sulfonate (Lodyne) in AFFF-Amended Microcosms. *Environmental Science & Technology*, 2015, 49, 7666-7674.
- McGuire, M.E. Schaefer, C.; Richards, T.; Backe, W.J.; Field, J.A.; Houtz, E.F.; Sedlak, D.L.; Guelfo, J.L.; Wunsch, A.; Higgins, C.P. An In-Depth Site Characterization of Poly- and Perfluoroalkyl Substances at an Abandoned Fire Training Area. *Environmental Science & Technology*, 2014, 48, 6644-6652.
- Houtz, E.F., Higgins, C.P., Field, J.A., Sedlak, D.L. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environmental Science & Technology*, 2013, 47, 8187-8195.
- Houtz, E.F.; Sedlak, D.L. Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff. *Environmental Science & Technology*, 2012, 46, 9342-9349.

## Ask The Expert Webinar Series

# TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

**Thank you for attending**

## **Closing the PFAS Mass Balance: The Total Oxidizable Precursor (TOP) Assay**

To submit a question, type it into the Questions panel in the GoToWebinar toolbar and click Send.

If you have any additional questions for today's presenter you may submit them directly to:

<http://testamericainc.com/services-we-offer/ask-the-expert/karla-buechler/>

Please be sure to visit the Ask the Expert Webinar Series web page for other scheduled webinars at:

<http://testamericainc.com/services-we-offer/webinars/upcoming-webinars/>

To view a recording of this webinar session, please contact:

[info@testamericawebinars.com](mailto:info@testamericawebinars.com)